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(54) Title of the Invention: ALKALINE BATTERY AND NEGATIVE ELECTRODE ACTIVE MATERIAL THEREOF

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(72) Inventor:	NAKAMURA KIYONOBU 1532-15 Takehara-cho, Takehara-shi, Hiroshima-ken
(72) Inventor:	UEMURA TOYOHIDE 652-15 Takehara-cho, Takehara-shi, Hiroshima-ken
(72) Inventor:	INOUE HIDETOSHI 1533-1, Takehara-cho, Takehara-shi, Hiroshima-ken
(71) Applicant:	MITSUI MINING & SMELTING CO LTD 2-1-1 Nihonbashi Muro-machi Chuo-ku Tokyo
(74) Agent:	ITO TATSUO, Patent Attorney and one other

SPECIFICATION

1. Title of the Invention

Alkaline Battery and Negative Electrode Active Material Thereof

2. Scope of Claims

1. An alkaline battery having zinc alloy powder and an electrolyte, which contains a negative electrode material in which polyglyceryl fatty acid ester at 0.001 to 1.0 parts by weight is added to said zinc alloy powder at 100 parts by weight.

2. A negative electrode active material for an alkaline battery, which is formed by covering the surface of said zinc alloy powder with polyglyceryl fatty acid ester at 0.001 to 0.1 parts by weight relative to zinc alloy powder at 100 parts by weight.

3. Detailed Description of the Invention

[Field of Industrial Application]

The present invention relates to an alkaline battery and a negative electrode active material thereof. In particular it relates to an alkaline battery and a negative electrode active material thereof, in which the amount of hydrogen gas evolution is reduced significantly by adding polyglyceryl fatty acid ester at 0.001 to 0.1 part by weight to zinc alloy powder, which is used as a negative electrode active material, at 100 parts by weight, or to an alkaline water solution, being an electrolyte, and also the battery performance is improved.

[0004]

[Prior Art]

In an alkaline battery or the like, in which zinc is used as a negative electrode active material, since a strong alkaline electrolyte is used, such as a potassium hydroxide solution or the like, the battery must be sealed. This sealing of the battery is important, especially when aiming to miniaturize the battery. However, it means at the same time that hydrogen gas evolution due to the corrosion of zinc must be confined during storage of the battery. Accordingly, the pressure of the gas inside the battery increases during long term storage, so that the more completely it is sealed, the more dangers such as that of explosion arise.

[0005]

To deal with this, research has been performed to prevent zinc, being a negative electrode active material, from corroding, so as to decrease the hydrogen gas evolution inside the battery, and amalgamated zinc in which the hydrogen overvoltage of zinc is utilized has been solely used as a negative electrode active material. As a result, the negative electrode active material of alkaline batteries on the market contains a large amount of mercury at approximately 3.0 percent by weight. The development of a battery with lower mercury content or no mercury has been strongly expected as a social demand.

[0006]

Therefore, a range of proposals has been made regarding a zinc alloy powder in which a range of metals is added to zinc in order to reduce the mercury content in a battery. For example, there are a zinc alloy powder in which lead is added to mercury, a zinc alloy powder in which lead and indium are added to zinc (Japanese Unexamined Patent Publication No. Sho 58-181266), and the like. Furthermore, a zinc alloy powder is also proposed in which potassium, aluminum, and the like, are added.

[0007]

[Problems that the Invention is to Solve]

In this manner, by using a zinc alloy powder, it is possible to retard the hydrogen gas evolution reliably even if the mercury content is reduced to some extent. However, on the other hand, when the mercury content is significantly reduced, an accompanying problem of deterioration in the discharge performance is manifested. That is, when the mercury content of a zinc alloy powder is reduced to approximately 0.1 to 0.2% in response to social demand, the incidence rate of hydrogen gas increases by approximately 4 to 5 times in comparison with existing **[powder]** with a mercury content of approximately 3.0 percent by weight. Moreover, the discharge performance deteriorates to approximately 80%.

[0008]

The cause of this can be considered to be as follows.

[0009]

That is, the following can be considered as the effects of the mercury in a battery.

(1) It aids electrical contact between zinc alloy powder particles.

(2) It suppresses the generation of a passivation film on the surface of the zinc alloy powder particles, and has an effect on the homogeneous dissolution of zinc.

(3) It improves the corrosion resistance of zinc, and prevents the electrical contact between the zinc alloy powder particles from being obstructed by the hydrogen gas bubbles generated accompanying the corrosion of zinc.

[0010]

However, in the case where the mercury content of zinc alloy powder particles reaches an extremely low mercury content, which is less than or equal to 0.2 percent by weight, it is considered that since the specific effects of mercury in item (3) cannot be exhibited sufficiently, the discharge performance deteriorates.

[0011]

The present invention takes the above situation into consideration, with an object of providing an alkaline battery and a negative electrode active material thereof, in which the hydrogen gas evolution is retarded while the percentage content of mercury is reduced, and also the discharge performance is maintained at a high level.

[0012]

[Means of Solving the Problem]

The present inventors accomplished the present invention by finding, as a result of keen research in accordance with the objects, that by adding a specified amount of polyglyceryl fatty acid ester to a negative electrode active material formed from zinc alloy powder, or an electrolyte formed from an alkaline water solution, an alkaline battery can be obtained in which the hydrogen gas evolution is retarded significantly in comparison with one that has no polyglyceryl fatty acid ester added, and the discharge performance is improved.

[0013]

That is, an alkaline battery of the present invention is an alkaline battery that has zinc alloy powder and an electrolyte, and has a negative electrode material, in which polyglyceryl fatty acid ester at 0.001 to 1.0 part by weight is added to the zinc alloy powder at 100 parts by weight.

[0014]

Hereunder is a further detailed description of the present invention.

[0015]

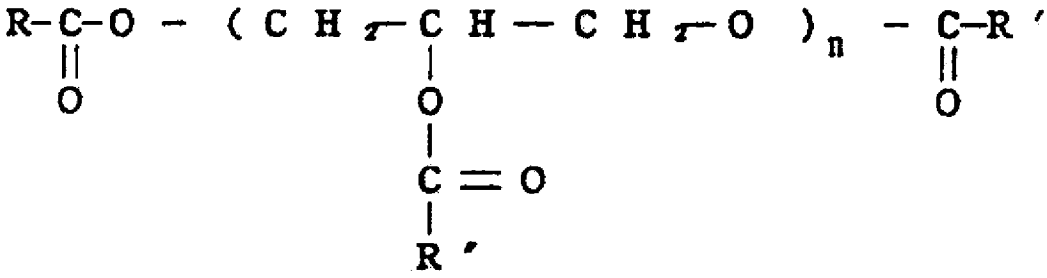
In the present invention, a zinc alloy powder used as a negative electrode active material is one that contains, for example, at least a certain amount of one of the following, starting with lead and aluminum, indium, magnesium, calcium, cadmium, tin, potassium, nickel, silver and the like. For a method of producing the zinc alloy powder, for example, a powder is used that is obtained by adding a prescribed amount of additional elements such as lead, aluminum, and the like, in a zinc melt as required, mixed and alloyed, and afterwards atomized by compressed air, pulverized and then sifted, and selected by size. The content of each of the additional elements in the zinc alloy powder is typically 0.001 to 0.5 percent by weight.

[0016]

In the present invention, when manufacturing the above-described zinc alloy powder, it may be acceptable to use amalgamated zinc alloy powder obtained by further adding a desired amount of mercury, amalgamated zinc alloy powder obtained by dry-amalgamating the zinc alloy powder with a desired amount of mercury using a V type mill, a rotation drum, or the like, for example, or an amalgamated zinc alloy powder obtained by wet-amalgamating the zinc alloy powder with a desired amount of mercury in a dilute alcohol solution such as potassium hydroxide, sodium hydroxide, or the like, for example. In this case, it is desirable that the percentage content of the mercury in the amalgamated zinc alloy powder is less than before, that is less than or equal to 3.0 percent by weight. However, considering low pollution, it is further desirable to be less than or equal to 1.5 percent by weight.

[0017]

Furthermore, it is most preferable that a polyglyceryl fatty acid ester used in the present invention is one that is expressed by the following general expression.



[0018]

R, R' and R" in the above expression each designate any one of the types of H, an alkyl group, and an alkenyl group, and R, R'and R" may be the same or different. Here, for R", there are n (R_1" to R_n") depending on the value of n in the above expression, and these may also be the same or different. Here, the preferred range for the number of carbons in the groups expressed by R, R' and R" is 1 to 20. To be specific, an alkyl group such as a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, heptadecyl group, an octadecyl group, a nonadecyl group, an eicosyl group and the like, and an alkenyl group such as a cis-9- heptadecyl group and the like, can be listed. In particular, a heptadecyl group is preferable.

[0019]

Moreover, n in the general expression designates an integer number of greater than or equal to 1, and preferably 6.

[0020]

The polyglyceryl fatty acid ester used in the present invention may be one type of polyglyceryl fatty acid ester, or a mixture of two or more types.

[0021]

In an alkaline battery of the present invention, the above-described polyglyceryl fatty acid ester is added to the zinc alloy powder and a negative electrode material having an electrolyte such as a potassium hydroxide water solution or the like. For the method of addition, examples of methods can be given in which zinc alloy powder is coated with polyglyceryl fatty acid ester, and it is then used as a negative electrode active material, or it is added to an electrolyte such as a potassium hydroxide water solution, a sodium hydroxide water solution or the like, or a gelling agent. However, in the present invention, it is most desirable from the points of retarding hydrogen gas evolution, and improving the discharge performance, to insert and mix zinc alloy powder in a solvent of toluene in which polyglyceryl fatty acid ester is added, and afterwards to dry and volatize the solvent to form a coating layer of polyglyceryl fatty acid ester on the surface of the zinc alloy powder, and use it as a negative electrode active material.

[0022]

In the present invention, the zinc alloy powder on the surface of which the above-described coating layer of polyglyceryl fatty acid ester is formed may also be amalgamated using a similar method to the aforementioned method of amalgamating zinc alloy powder, forming for use a coating layer in a state in which polyglyceryl fatty acid ester and mercury are mixed on the surface of the zinc alloy powder. Furthermore, mercury may also be added to and mixed in an electrolyte to form a negative electrode material together with the zinc alloy powder on the surface of which the coating layer of polyglyceryl fatty acid ester is formed.

[0023]

The additional amount of the polyglyceryl fatty acid ester added into the negative electrode material is 0.001 to 1.0 part by weight relative to the zinc alloy powder at 100 parts by weight. If the additional amount of the polyglyceryl fatty acid ester is less than 0.001 part by weight, the effects of the present invention, of improving the corrosion resistance of zinc and retarding hydrogen gas evolution, cannot be obtained. If it exceeds

1.0 part by weight, during discharging the polyglyceryl fatty acid ester in the coating layer of polyglyceryl fatty acid ester formed on the surface of the zinc alloy powder in the electrolyte, and the like, becomes a barrier, so that the dissolution reaction of zinc is inhibited. Therefore excellent discharge performance cannot be obtained.

[0024]

These working effects due to polyglyceryl fatty acid ester are not determined sufficiently. However, it is assumed that since polyglyceryl fatty acid ester sticks to the surface of the zinc allow powder, and works as an inhibitor during the **storage of a battery**, there is an effect of improving the corrosion resistance, and hydrogen gas evolution accompanying the corrosion of zinc is retarded, and furthermore, adverse effects such as inhibiting electrical contact between zinc alloy powder particles due to hydrogen gas bubbles, which is conventionally seen during discharge, is suppressed, so that the discharge performance is improved.

[0025]

[Example]

Hereunder is a specific description of the present invention based on examples and comparative examples.

[0026]

Examples 1 to 5 and Comparative Examples 1 to 3

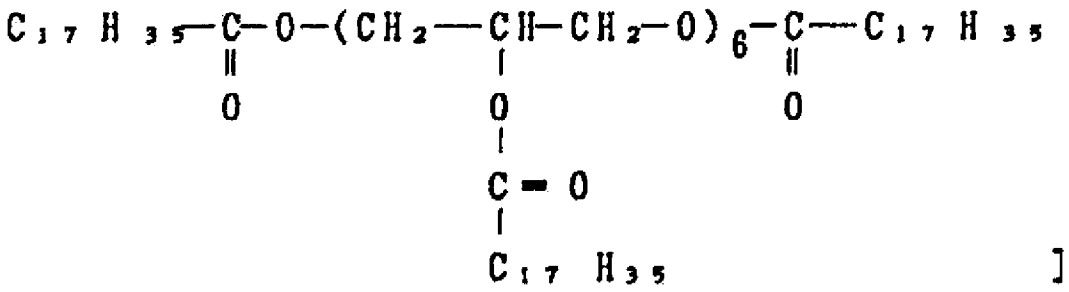
Zinc metal with a purity of 99.997% or greater was melted at approximately 500°C, each of the elements shown in Table 1 excluding mercury was added to it to produce a zinc alloy, and it was pulverized using high pressure argon gas. The powder was sifted to a range of grain sizes of 50 to 150 mesh to obtain zinc alloy powder.

[0027]

Next, mercury was added to the above-described powder in an alkaline water solution with 10% potassium hydroxide so as to get the content shown in Table 1, amalgamate processing was performed, and the amalgamated zinc alloy powder as shown in Table 1 was obtained.

[0028]

Next, in a toluene solvent in which polyglyceryl fatty acid ester [made by NOF Corporation, Product Name: Unigly GS-106, Composition: hexaglycerin ester stearate;



was added and dissolved, the amalgamated zinc alloy powder was dropped in and the toluene was dried and volatilized during mixing, a coating layer of polyglyceryl fatty acid ester with a ratio as shown in Table 1 was formed on the surface of the amalgamated zinc alloy powder, and a negative electrode active material was produced.

[0029]

Furthermore, an electrolyte was produced by adding carboxymethyl cellulose and sodium polyacrylate as gelling agents at approximately 1.0% to potassium hydroxide water solution at 40 percent concentration, which was saturated with zinc oxide.

[0030]

A negative electrode material was formed by mixing 3.0g of the negative electrode active material and 1.8g of the electrolyte obtained above into a gel state. Moreover, a positive electrode material was formed by mixing manganese dioxide and a conductive agent. By using the negative electrode material and the positive electrode material, an alkaline manganese battery as shown in FIG. 1 was produced, and a test was performed.

[0031]

The alkaline manganese battery of FIG. 1 comprises a positive electrode can 1, a positive electrode 2, a negative electrode (amalgamated zinc alloy powder which was made into a gel state) 3, a separator 4, a sealing **piece** 5, a negative electrode base plate 6, a negative electrode collector 7, a cap 8, a heat shrink resin tube 9, insulating rings 10 and 11, and an outer packaging can 12.

[0032]

Using the alkaline manganese battery, the discharge duration time until a final voltage of 0.9V was reached was measured under discharge conditions of a discharge load of 2Ω at 20°C, and shown as an index based on the measured value of a comparative example 1, using a conventional negative electrode material not including polyglyceryl fatty acid ester, being 100. The results are shown in Table 1.

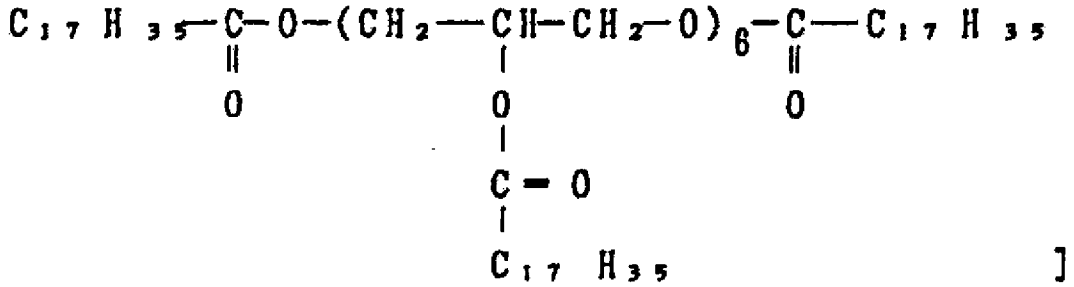
[0033]

Furthermore, using the above negative electrode material, the gas evolution rate (ml/g. day) at 60°C was measured for 20 days, and the results are listed in Table 1 as an index based on the measured value of a comparative example 1, using a conventional negative electrode material not including polyglyceryl fatty acid ester, being 1.00.

[0034]

Example 6

The discharge duration time and the gas evolution rate were measured using a similar method to example 2, except that after forming a coating layer of polyglyceryl fatty acid ester in the proportions shown in Table 1 on the surface of non amalgamated zinc alloy powder similar to that in example 2 employing polyglyceryl fatty acid ester [made by NOF Corporation, Product Name: Unigly GS-106, Composition: hexaglycerin ester stearate;

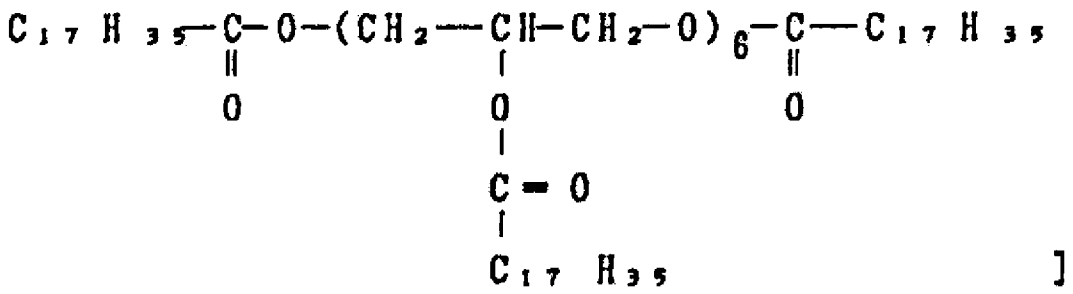


using a similar method to example 2 but without applying amalgamation processing, amalgamation treatment was applied so as to achieve the proportions shown in Table 1 using a similar method to example 2, and the resultant was used as a negative electrode active material. The results are listed in Table 1.

[0035]

Example 7

The discharge duration time and the gas evolution rate were measured using a similar method to example 2, except that after forming a coating layer of polyglyceryl fatty acid ester in the proportions shown in Table 1 on the surface of non amalgamated zinc alloy powder similar to that in example 2 employing polyglyceryl fatty acid ester [made by NOF Corporation, Product Name: Unigly GS-106, Composition: hexaglycerin ester stearate;

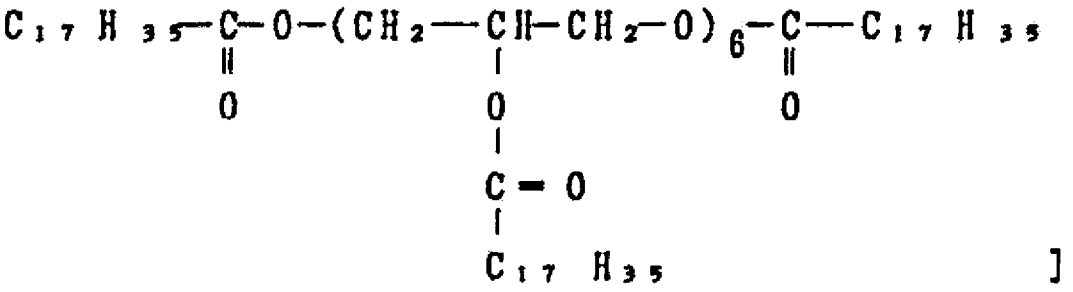


using a similar method to example 2 but without applying amalgamation processing, 3.0g of the obtained negative electrode active electrode material and 3.0mg of mercury were added to 1.8g of electrolyte similar to that in example 2, and mixed into a gel state to form a negative electrode material. The results are listed in Table 1.

[0036]

Example 8

The discharge duration time and the gas evolution rate were measured using a similar method to example 2, except that 3.0g of amalgamated zinc alloy powder similar to that in example 2, and 3.0mg of polyglyceryl fatty acid ester [made by NOF Corporation, Product Name: Unigly GS-106, Composition: hexaglycerin ester stearate;



were added to 1.8g of electrolyte similarly to example 2, mixed into a gel state to form a negative electrode material, and the results are listed in Table 1.

[0037]

Table 1

Example Comparative Example	Additive amount of polyglyceryl fatty acid ester (parts by weight) *1	Composition of zinc alloy powder	Discharge time (index)	Gas evolution rate (index)
Example 1	0.001 (coating)	**See Jap original**	125	0.18
Example 1	0.1 (coating)	**See Jap original**	127	0.15

Example 1	1.0 (coating)	**See Jap original**	126	0.14
Example 1	0.1 (coating)	**See Jap original**	126	0.18
Example 1	0.1 (coating)	**See Jap original**	127	0.10
Example 6 *2	0.1 (coating)	**See Jap original**	128	0.13
Example 7 *3	0.1 (coating)	**See Jap original**	128	0.14
Example 8	0.1 (mixed)	**See Jap original**	100	0.18
Comparative Example 1	-	**See Jap original**	98	1.00
Comparative Example 2	-	**See Jap original**	125	1.45
Comparative Example 3	-	**See Jap original**		0.35

*1: Amount relative to the above zinc alloy powder at 100 parts by weight.

*2: After coating non-amalgamated zinc alloy powder with polyglyceryl fatty acid ester, amalgamate processing was performed.

*3: After coating non-amalgamated zinc alloy powder with polyglyceryl fatty acid ester, mercury was added to the electrolyte such that it had 0.1 percent by weight of zinc alloy powder.

[0038]

As shown in Table 1, examples 1 to 4 used a negative electrode material whose negative electrode active material was amalgamated zinc alloy powder with a mercury content of 0.1 percent by weight coated with polyglyceryl fatty acid ester, and the hydrogen gas evolution rate was significantly reduced regardless of the difference in the composition of the amalgamated zinc alloy powder serving as a negative electrode active material, compared with comparative examples 1 and 2 in which polyglyceryl fatty acid ester was not added to the negative electrode material, and furthermore alkaline batteries incorporating this negative electrode material had excellent discharge performance.

[0039]

Moreover, in example 5, a negative electrode material was used whose negative electrode active material was amalgamated zinc alloy powder with a mercury content of 1.0 percent by weight, coated with polyglyceryl fatty acid ester. In this case also, compared with comparative example 3 in which polyglyceryl fatty acid ester was not

added to the negative electrode active material, the discharge performance of an alkaline battery incorporating this negative electrode active material was improved, and the hydrogen gas evolution rate was significantly reduced.

[0040]

Furthermore, in example 6, a negative electrode material was used whose negative electrode active material was formed by applying amalgamate processing after coating the surface of non-amalgamated zinc alloy powder with polyglyceryl fatty acid ester. In this case also, the hydrogen gas evolution rate was significantly reduced, and an alkaline battery incorporating this negative electrode active material had an excellent discharge performance.

[0041]

In example 7, a negative electrode material was used that was obtained from a negative electrode active material formed by coating the surface of non-amalgamated zinc alloy powder with polyglyceryl fatty acid ester, adding it to an electrolyte with mercury, and mixing. In this case also, a significant reduction in the hydrogen gas evolution rate, and an improvement in the discharge performance of an alkaline battery incorporating this negative electrode material were prominent.

[0042]

In example 8, a negative electrode material was used that was formed by adding and mixing a specified amount of polyglyceryl fatty acid ester into an alkaline water solution, which was an electrolyte. In this case as well, there was an effect of retarding the hydrogen gas evolution, and furthermore, there was also an effect of improving the discharge performance of an alkaline battery incorporating this negative electrode material.

[0043]

As described above, using an alkaline battery of the present invention, which has a negative electrode material to which a specified amount of polyglyceryl fatty acid ester is added, in the case where the mercury content is lower than conventionally, specifically, even in the case of an ultra-low amount of mercury, in which the mercury content is 0.2 percent by weight or less of the zinc alloy powder used, the hydrogen gas evolution in the battery is retarded significantly, and also the battery performance is improved. Furthermore, since the mercury content can be lower than conventionally, it also satisfies a social demand. In particular, by using a negative electrode active material in which zinc

alloy power is coated with a specified amount of polyglyceryl fatty acid ester, the effects are even more prominent.

[0044]

Brief Description of the Drawings

FIG. 1 shows a sectional side view of an alkaline manganese battery according to the present invention.

1: Positive Electrode Can

2: Positive Electrode

3: Negative Electrode

4: Separator

5: Sealing Piece

6: Negative Electrode Base Plate

7: Negative Electrode Collector

8: Cap

9: Heat Shrink Resin Tube

10, 11: Insulating Ring

12: Outer Packaging Can

FIGURE 1

⑲日本国特許庁(JP)　⑪特許出願公開

⑫公開特許公報(A)　平2−135666

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	4/06	T	8222−5H	

審査請求　未請求　請求項の数 2　(全6頁)

⑤発明の名称　アルカリ電池およびその負極活物質

⑳特　願　昭63−287737

㉒出　願　昭63(1988)11月16日

㉗発明者　中村　精伸　広島県竹原市竹原町1532−15

㉗発明者　植村　豊秀　広島県竹原市竹原町652−15

㉗発明者　井上　秀利　広島県竹原市竹原町1533−1

㉑出願人　三井金属鉱業株式会社　東京都中央区日本橋室町2丁目1番1号

㉔代理人　弁理士　伊東　辰雄　外1名

明　細　書

1．発明の名称

アルカリ電池およびその負極活物質

2．特許請求の範囲

1．亜鉛合金粉末、電解液を有し、該亜鉛合金粉末100重量部に対して0.001〜1.0重量部のポリグリセリン脂肪酸エステルを添加した負極材を有するアルカリ電池。

2．亜鉛合金粉末100重量部に対して0.001〜1.0重量部のポリグリセリン脂肪酸エステルを該亜鉛合金粉末の表面に被覆して成るアルカリ電池用負極活物質。

3．発明の詳細な説明

［産業上の利用分野］

本発明はアルカリ電池およびその負極活物質に関し、詳しくは負極活物質として用いられる亜鉛合金粉末または電解液であるアルカリ水溶液等にポリグリセリン脂肪酸エステルを該亜鉛合金粉末100重量部に対して0.001〜1.0重量部添加することにより、水素ガス発生量が著しく抑制され、しかも電池性能が向上されたアルカリ電池およびその負極活物質に関する。

［従来の技術］

亜鉛を負極活物質として用いたアルカリ電池等においては、水酸化カリウム水溶液等の強アルカリ性電解液を用いるため、電池を密閉しなければならない。この電池の密閉は電池の小型化を図る際には特に重要であるが、同時に電池保存中の亜鉛の腐食により発生する水素ガスを閉じ込めることになる。従って長期保存中に電池内部のガス圧が高まり、密閉が完全なほど爆発等の危険が伴なう。

その対策として、負極活物質である亜鉛の腐食を防止して、電池内部の水素ガス発生を少なくすることが研究され、水銀の水素過電圧を利用した汞化亜鉛を負極活物質として用いることが専ら行なわれている。このため、今日市販されているアルカリ電池の負極活物質は3.0重量%程度の多量の水銀を含有しており、社会的ニーズとして、より低水銀のもの、あるいは無水銀の電池の開発が

強く期待されるようになってきた。

そこで、電池内の水銀含有量を低減させるべく、亜鉛に各種金属を添加した亜鉛合金粉末に関する提案が種々なされている。例えば、亜鉛に鉛を添加した亜鉛合金粉末、あるいは亜鉛に鉛とインジウムを添加した亜鉛合金粉末（特開昭 58-181266 号公報）等がある。またガリウム、アルミニウム等を添加した亜鉛合金粉末も提案されている。

［発明が解決しようとする課題］

このように亜鉛合金粉末を用いることにより、確かに水銀含有量をある程度低減させても水素ガス発生を抑制させることが可能となったが、一方では水銀含有量を著しく低減させた際に伴なう放電性能の劣化という課題が顕在化してきた。即ち、社会的ニーズに対応して亜鉛合金粉末の水銀含有量を 0.1～ 0.2重量%程度に低減させると、従来の 3.0重量%程度の水銀含有量のものと比較して水素ガス発生率が 4～5 倍程度に増大してしまうと共に、放電性能が80%程度まで劣化してしまう。

この原因としては次のことが考えられる。

即ち、電池内における水銀の作用としては以下のことが考えられる。

(1)亜鉛合金粉末粒子間の電気的接触を助ける。

(2)亜鉛合金粉末粒子表面に不働態化被膜が生成するのを抑制し、亜鉛の均一溶解に効果がある。

(3)亜鉛の耐食性を向上させ、亜鉛の腐食に伴なって生成する水素ガス気泡により亜鉛合金粉末粒子間の電気的接触が阻害されるのを抑制する。

しかるに、亜鉛合金粉末の水銀含有量が 0.2重量%以下という超低水銀量になった場合、特に第(3) 項の水銀の作用が充分に発揮されなくなってくるために放電性能が劣化すると考えられる。

本発明はかかる現状に鑑み、水銀の含有率を著しく減少させつつ、水素ガス発生が抑制され、しかも放電性能が高い水準に維持されたアルカリ電池およびその負極活物質を提供することを目的とする。

［課題を解決するための手段］

本発明者らは、この目的に沿って鋭意研究の結果、亜鉛合金粉末から成る負極活物質またはアルカリ水溶液から成る電解液等にポリグリセリン脂肪酸エステルを特定量添加することにより、ポリグリセリン脂肪酸エステルを無添加のものに比べて著しく水素ガス発生が抑制され、しかも放電性能が向上されたアルカリ電池が得られることを見出し本発明に到達した。

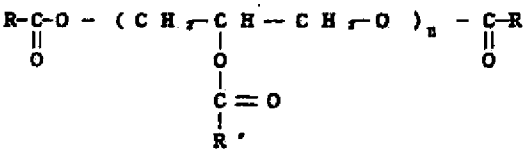
すなわち、本発明のアルカリ電池は、亜鉛合金粉末、電解液を有し、該亜鉛合金粉末 100重量部に対して 0.001～ 1.0重量部のポリグリセリン脂肪酸エステルを添加した負極材を有するアルカリ電池にある。

以下、本発明を更に詳細に説明する。

本発明において、負極活物質として用いられる亜鉛合金粉末としては、鉛やアルミニウムを始めとしてインジウム、マグネシウム、カルシウム、カドミウム、錫、ガリウム、ニッケル、銀等のうちの少なくとも一種が一定量含有されたものが例示される。この亜鉛合金粉末の製造方法としては、例えば亜鉛溶湯中に、所望により鉛、アルミニウム等の添加元素を所定量添加し、撹拌して合金化させた後、圧縮空気によりアトマイズし、粉体化させ、さらに篩い分けを行なって整粒して得られた粉末を用いる。この亜鉛合金粉末中の各添加元素の含有率は、 0.001～ 0.5重量%が一般的である。

本発明においては、上記亜鉛合金粉末の製造の際に所望量の水銀をさらに添加して得られる汞化亜鉛合金粉末、上記亜鉛合金粉末を例えばV型ミルまたは回転ドラム等を用いて所望量の水銀で乾式汞化して得られる汞化亜鉛合金粉末、もしくは上記亜鉛合金粉末を例えば水酸化カリウム、水酸化ナトリウム等の希アルカリ溶液中で所望量の水銀で湿式汞化して得られる汞化亜鉛合金粉末を用いてもよく、この場合、汞化亜鉛合金粉末中の水銀含有率は従来より少ない量、すなわち 3.0重量%以下であることが望ましいが、低公害性を考慮すると 1.5重量%以下であることがさらに望ましい。

また、本発明において用いられるポリグリセリン脂肪酸エステルとしては、下記一般式



で表されるものが最も好ましく用いられる。

上式中のR，R′，R″はH，アルキル基，アルケニル基のうちのいずれか一種を示し、R，R′，R″は同一または異なってもよい。なお、R″としては上式中のnの数によってn個（R₁″～Rₙ″）存在するが、これらも同一または異なってもよい。ここでR，R′，R″で表される基の炭素数の好ましい範囲は1～20であり、具体的にはメチル基、エチル基、プロピル基、ブチル基、ペンチル基、ヘキシル基、ヘプチル基、オクチル基、ノニル基、デシル基、ウンデシル基、ドデシル基、トリデシル基、テトラデシル基、ペンタデシル基、ヘキサデシル基、ヘプタデシル基、オクタデシル基、ノナデシル基、エイコシル基等のアルキル基、あるいはcis-9-ヘプタデセニル基等のアルケニル基が挙げられ、特に好ましくはヘプタデシル基である。

また、前記一般式中のnは1以上の整数を示し、好ましくは6である。

なお、本発明において用いられるポリグリセリン脂肪酸エステルは、1種類のポリグリセリン脂肪酸エステルであっても、あるいは2種以上の混合物であってもよい。

本発明のアルカリ電池にあっては、前記亜鉛合金粉末と水酸化カリウム水溶液等の電解液を有する負極材中に、上述のポリグリセリン脂肪酸エステルを添加する。添加する方法としては、亜鉛合金粉末にポリグリセリン脂肪酸エステルを被覆させ、これを負極活物質として用いるか、あるいは水酸化カリウム水溶液、水酸化ナトリウム水溶液等の電解液またはゲル化剤に添加する方法等が例示されるが、本発明にあってはポリグリセリン脂肪酸エステルを添加したトルエン等の溶媒中に亜鉛合金粉末を入れて混合した後、溶媒を乾燥揮発させることによって亜鉛合金粉末表面にポリグリセリン脂肪酸エステルのコーティング層を形成させ、これを負極活物質として用いることが、水素ガス発生抑制効果、放電性能の向上効果の点から最も好ましい。

なお、本発明にあっては、上記のポリグリセリン脂肪酸エステルのコーティング層を表面に形成させた亜鉛合金粉末を、前述の亜鉛合金粉末を汞化する方法と同様の方法によって汞化して、亜鉛合金粉末表面にポリグリセリン脂肪酸エステルと水銀とが混在した状態のコーティング層を形成させて用いてもよい。また、上述のポリグリセリン脂肪酸エステルのコーティング層を表面に形成させた亜鉛合金粉末と共に負極材を形成する電解液中に水銀を添加、混合して用いてもよい。

ここで負極材中に添加するポリグリセリン脂肪酸エステルの添加量は、上記亜鉛合金粉末100重量部に対して0.001～1.0重量部である。ポリグリセリン脂肪酸エステルの添加量が0.001重量部未満では亜鉛の耐食性を改善して水素ガス発生を防止するといった本発明の効果が得られず、1.0重量部を超えた場合には放電時に、亜鉛合金粉末表面上に形成させたポリグリセリン脂肪酸エステルのコーティング層中、電解液中等に存在するポリグリセリン脂肪酸エステルがバリヤーとなって亜鉛の溶解反応が阻害される等して良好な放電性能が得られない。

これらポリグリセリン脂肪酸エステルによる作用効果は充分に解明されていないが、推定するに、電池の保存中はポリグリセリン脂肪酸エステルが亜鉛合金粉末の表面に吸着してインヒビターとして働くために亜鉛の耐食性の向上に効果があり、亜鉛の腐食に伴なう水素ガス発生が抑制され、さらに、放電時において従来見られた水素ガス気泡による亜鉛合金粉末粒子間の電気的接触の阻害といった悪影響が抑制される等によって放電性能が向上するものと考えられる。

[実施例]

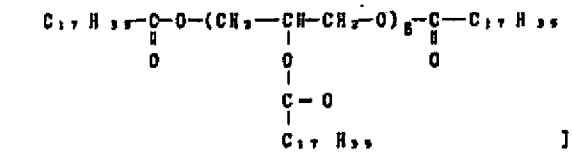
以下、実施例および比較例に基づいて本発明を具体的に説明する。

実施例１～５および比較例１～３

純度99.997%以上の亜鉛地金を約 500℃で溶融し、これに水銀を除いた第１表に示す各元素を添加して亜鉛合金を作成し、これを高圧アルゴンガス（噴出圧 5kg／cm²）を使って粉体化した。この粉体を50～ 150メッシュの粒度範囲に篩い分けして亜鉛合金粉末を得た。

次に水酸化カリウム10%のアルカリ性溶液中にて上記粉末に第１表に示す含有割合となるように水銀を添加して、汞化処理を行なって第１表に示す汞化亜鉛合金粉末を得た。

次に、ポリグリセリン脂肪酸エステル［日本油脂㈱製、商品名：ユニグリGS-106、組成：ヘキサグリセリンステアリン酸エステル；



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を添加し、溶解させたトルエン溶媒中に上記の汞化亜鉛合金粉末を投入し、混合しながらトルエンを乾燥揮発させ、汞化亜鉛合金粉末の表面に第１表に示す割合のポリグリセリン脂肪酸エステルのコーティング層を形成させ、負極活物質とした。

また、濃度40%の水酸化カリウム水溶液に酸化亜鉛を飽和させたものにゲル化剤としてカルボキシメチルセルロースとポリアクリル酸ソーダを1.0%程度加えて電解液を作成した。

上記で得られた負極活物質 3.0gおよび電解液 1.8gを混合してゲル状化したものを負極材とした。また、二酸化マンガンと導電剤を混合して正極材とした。これらの負極材と正極材を用いて、第１図に示すアルカリマンガン電池を作成して試験を行なった。

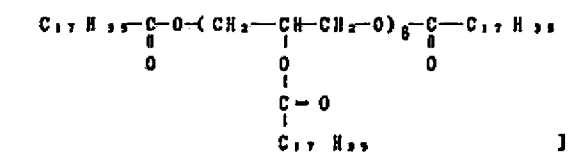
第１図のアルカリマンガン電池は、正極缶１、正極２、負極（ゲル状化した汞化亜鉛合金粉末）３、セパレーター４、封口体５、負極底板６、負極集電体７、キャップ８、熱収縮性樹脂チューブ９、絶縁リング10，11、外装缶12で構成されている。

このアルカリマンガン電池を用いて放電負荷 2Ω、20℃の放電条件により終止電圧 0.9Vまでの放電持続時間を測定し、ポリグリセリン脂肪酸エステルを含まない従来の負極材を用いた比較例１の測定値を 100とした指数で示した。その結果を第１表に示した。

また、上記負極材を用いて60℃で20日間のガス発生率（㎖／g・day）を測定し、その結果をポリグリセリン脂肪酸エステルを含まない従来の負極材を用いた比較例１の測定値を1.00とした指数で第１表に併記した。

実施例６

実施例２におけるものと同様の未汞化の亜鉛合金粉末の表面に、汞化処理を施さずに実施例２と同様の方法でポリグリセリン脂肪酸エステル［日本油脂㈱製、商品名：ユニグリGS-106、組成：ヘキサグリセリンステアリン酸エステル；



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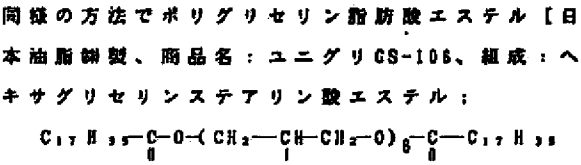
を用いて第１表に示す割合のポリグリセリン脂肪酸エステルのコーティング層を形成させた後に、同じく実施例２と同様の方法で第１表に示す割合となるように汞化処理を施して得られたものを負極活物質として用いた以外は実施例２と同様の方法で放電持続時間およびガス発生率の測定を行ない、それぞれの結果を第１表に併記した。

実施例７

実施例２におけるものと同様の未汞化の亜鉛合金粉末の表面に、汞化処理を施さずに実施例２と同様の方法でポリグリセリン脂肪酸エステル［日本油脂㈱製、商品名：ユニグリGS-106、組成：ヘキサグリセリンステアリン酸エステル；



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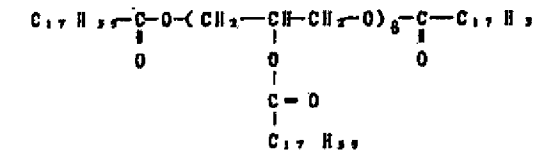
を用いて第１表に示す割合のポリグリセリン脂肪酸エステルのコーティング層を形成させて得られた負極活物質 3.0gと、水銀 3.0mgを、実施例２

と同様の電解液 1.8gに添加、混合してゲル状化したものを負極材とした以外は実施例2と同様の方法で放電持続時間およびガス発生率の測定を行ない、それぞれの結果を第1表に併記した。

実施例8

実施例2と同様の電解液 1.8gに、同じく実施例2におけるものと同様の汞化亜鉛合金粉末 3.0gとポリグリセリン脂肪酸エステル［日本油脂㈱製、商品名：ユニグリGS-106、組成：ヘキサグリセリンステアリン酸エステル；



］3.0mgを添加、混合してゲル状化したものを負極材とした以外は実施例2と同様の方法で放電持続時間およびガス発生率の測定を行ない、それぞれの結果を第1表に併記した。

第1表

実施例・比較例	ポリグリセリン脂肪酸エステルの添加量（重量部）※1	亜鉛合金粉末組成	放電時間（相対値）	ガス発生率（相対値）
実施例1	0.001（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	125	0.18
実施例2	0.1（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	127	0.15
実施例3	1.0（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	128	0.16
実施例4	0.1（重量）	Zn—0.06wt%Pb—0.06wt% In—0.1wt%Bi	128	0.18
実施例5	0.1（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—1.0wt%Bi	127	0.10
実施例6 ※2	0.1（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	127	0.11
実施例7 ※3	0.1（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In	128	0.34
実施例8 ※4	0.1（重量）	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	128	0.16
比較例1	—	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—0.1wt%Bi	100	1.00
比較例2	—	Zn—0.06wt%Pb—0.06wt% In—0.1wt%Bi	98	1.45
比較例3	—	Zn—0.06wt%Pb—0.06wt% Al—0.06wt%In—1.0wt%Bi	125	0.85

※1：上記亜鉛合金粉末 100重量部に対する量。
※2：ポリグリセリン脂肪酸エステルを未汞化亜鉛合金粉末に被覆した後、汞化処理を施したもの。
※3：ポリグリセリン脂肪酸エステルを未汞化亜鉛合金粉末に被覆し、水銀を亜鉛合金粉末の0.1重量%となるように電解液に添加したもの。

第1表に示されるごとく、ポリグリセリン脂肪酸エステルを水銀の含有割合が 0.1重量%である汞化亜鉛合金粉末に被覆したものを負極活物質とした負極材を用いた実施例1～4は、ポリグリセリン脂肪酸エステルを負極材に添加しなかった比較例1～2に比べて、負極活物質である汞化亜鉛合金粉末の組成の相違に拘らず、水素ガス発生率が著しく低減され、しかもこの負極材を組み込んだアルカリ電池は放電性能が優れていた。

また、実施例5は水銀の含有割合が 1.0重量%である汞化亜鉛合金粉末にポリグリセリン脂肪酸エステルを被覆したものを負極活物質とした負極材を用いたものであるが、この場合にもポリグリセリン脂肪酸エステルを負極材に添加しなかった比較例3に比べて、この負極材を組み込んだアルカリ電池の放電性能は向上し、水素ガス発生率が著しく低減された。

さらに、実施例6はポリグリセリン脂肪酸エステルを未汞化の亜鉛合金粉末の表面に被覆した後に汞化処理を施したものを負極活物質とした負極材を用いたものであるが、この場合にも水素ガス発生率が著しく低減され、しかもこの負極材を組み込んだアルカリ電池は放電性能が優れていた。

実施例7はポリグリセリン脂肪酸エステルを未汞化の亜鉛合金粉末の表面に被覆したものを負極活物質とし、水銀と共に電解液中に添加、混合して得られた負極材を用いたものであるが、この場合においても水素ガス発生率の著しい低減、この負極材を組み込んだアルカリ電池の放電性能の向上が顕著であった。

実施例8はポリグリセリン脂肪酸エステルを電解液であるアルカリ水溶液中に所定量を添加、混合した負極材を用いたものであるが、この場合にも水素ガス発生の抑制に効果があり、しかもこの負極材を組み込んだアルカリ電池における放電性能の向上にも効果があった。

［発明の効果］

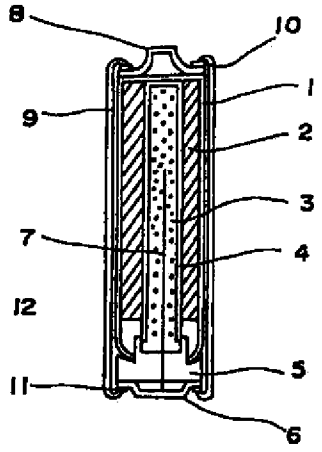
以上説明のごとく、特定量のポリグリセリン脂肪酸エステルを添加した負極材を有する本発明のアルカリ電池によれば、水銀の含有割合を従来よ

り低下させた場合、特に水銀の含有割合を用いる亜鉛合金粉末の 0.2重量%以下という超低水銀量とした場合においても、電池内における水素ガス発生が著しく抑制され、しかも電池性能が向上される。また、水銀を従来より低含有率にすることができるので社会的ニーズにも沿ったものである。特に、亜鉛合金粉末を特定量のポリグリセリン脂肪酸エステルで被覆した負極活物質を用いることによってその効果は一層顕著である。

4．図面の簡単な説明

第1図は本発明に係わるアルカリマンガン電池の側断面図を示す。

1：正極缶、　2：正極、　3：負極、
4：セパレーター、5：封口体、
6：負極底板、　7：負極集電体、
8：キャップ、　9：熱収縮性樹脂チューブ、
10，11：絶縁リング、　12：外装缶。



第　1　図